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## COMPLETE SPECIFICATION

## Production of Self-sealing Strips and Foils

- We, P. BEIERSDORF & Co., A. G., a German Company of Unnastrasse 48, Hamburg 20, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The invention relates to the production of self-sealing strips, and foils, more particularly medical plasters, by a process wherein an aqueous resin-containing mixture is applied to a flexible carrier sheet and becomes a pressure-sensitive adhesive layer after drying.
- It is known to use polymers of vinyl ethers or polymers of acrylic acid derivatives as self-sealing compositions. It is also known to use mixtures of vinyl ether polymers or copolymers and polymers or copolymers of acrylic acid derivatives. Such mixtures can be used in the form of aqueous dispersions, optionally with the addition of fillers and plasticisers, and applied to the carrier material by appropriate applicators.
- Unfortunately, these self-sealing composition and the adhesive products obtained by their use are not completely satisfactory. Also, commercially available aqueous polyacrylic acid ester dispersions and mixtures thereof with one another or with commercially available aqueous polyvinyl ester dispersions often have, as well as other disadvantages, too low a viscosity to be spreadable by conventional methods and therefore often have to be used in admixture with natural or synthetic resins to achieve optimum adhesive force, rapid sticking properties and suitable plasticity and viscosity.
- Polymers dissolved in organic solvents can readily be mixed with natural or synthetic resins soluble in such solvents, but considerable time and power is required to work water-insoluble, more particularly solid, natural or synthetic resins into aqueous dispersions or emulsions of high polymers. For instance, in one known process a suspension of pre-pulverised resins is treated in a ball mill, together with other additives having an emulsifying action, for about 5 hours and only then mixed with the dispersion of a natural or synthetic rubber (latex). Three different working steps are therefore required to produce an adhesive composition of this kind, namely pulverisation of the resin, production of an aqueous resin dispersion and mixing thereof with the latex.
- In the known processes it is necessary to add emulsifiers to the composition or to add an alkaline substance e.g. ammonia, which forms a water-soluble soap with some resins and therefore also provides an emulsifying action. For many applications, however, the content of emulsifying agent in the dispersion mixtures should be only small since the emulsifying agents increase the sensitivity to water of the pressure-sensitive adhesive and this may have deleterious effects on the carrier after the coating has dried. Further the presence of alkali or ammonia in the product cannot be tolerated for some kinds of adhesive strip; for instance, medical plasters containing adhesive compositions having an alkaline reaction tend to affect the acid cortex of the skin and may cause alkali damage to the skin similar to the effect on the skin of many detergents.
- It is an object of the invention to provide a process for the preparation of self-adhesive strips and foils, more particularly medical plasters, having an adhesive layer free from ingredients having a detrimental action, more particularly an unwanted action on the substrate, such as human skin, in subsequent use.
- According to the present invention self-adhesive strips and foils, more particularly

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medical plasters, which are free from the disadvantages mentioned and which have very good properties, are produced by a process which comprises mixing with vigorous agitation a solid, water-insoluble resin or mixture of such resins having a softening point of 95°C or less, heated to a temperature above the said softening point, with an aqueous dispersion of a non-toxic, chemically neutral vinyl ether polymer or vinyl ether copolymer, mixing the mixture obtained with an aqueous dispersion of a polymer or copolymer of an acrylic acid derivative selected from polyacrylic acid esters, polymethacrylic acid esters, and copolymers of acrylic acid esters or methacrylic acid esters with other monomers copolymerisable therewith, applying the mixture thus obtained as a layer on a flexible carrier material and drying the layer thus obtained.

In a preferred form of the invention, from 2 to 50 parts by weight, preferably from 5 to 25 parts by weight, of the resin or resin mixture are mixed with from 20 to 50 parts by weight, (referred to the solids content) of the aqueous dispersion of the vinyl ether polymer or vinyl ether copolymer, and the mixture is mixed with from 25 to 75 parts by weight, (referred to the solids content) of the aqueous dispersion of the said polymer or copolymer of acrylic acid derivative.

These steps enable water-insoluble solid natural resins or synthetic resins or mixtures thereof having a softening point of up to 95°C to be worked into aqueous plastics dispersions or mixtures thereof in a single step and very rapidly, without the need to use organic solvents or an addition of emulsifiers and/or alkali or ammonia. Production costs therefore decrease considerably. Also, the process enables aqueous plastics dispersions to have worked into them solid, natural or synthetic resins having a softening point of above 100°C if water-insoluble, natural or synthetic resins having a lower melting point are added to the solid resins to an extent such that the softening point of the resulting mixture of natural or synthetic resins is reduced at least to 95°C.

The process of the invention makes it possible to produce plasters which cause less than half the skin irritation caused by the adhesive compositions used in conventional plasters and emergency wound dressings and which cause substantially no macerations.

Extensive research has shown that the skin irritation caused by the adhesive used in a medical plaster is mainly the result of organic solvent residues in the adhesive and such residues are in turn due to the conventional procedure for applying the adhesive composition from a solution in an organic solvent; contrary to what has hitherto been thought to be the case, the skin irritation is due at most to only a very small extent to the elastomers or resins used for the composition provided that

such elastomers or resins are chemically neutral and non-toxic compounds. Solvent residues can demage the skin in various ways. Organic solvents often have toxic properties, but besides this they attack the lipid cortex of the skin because of their ability to dissolve fat, and thus lower the ability of the skin to resist all forms of foreign influence. Also, even very small residues of organic solvents may help to transport toxic ingredients, such as impurities, of the plaster and by their presence help such substances to diffuse to the skin. Since it is very complicated and costly completely to dry medical plasters whose self-sealing composition has been applied from a solution in an organic solvent, particularly if the carrier used for the composition is impervious, great advantages attach to the production of medical plasters by the process according to the invention, since such a process does not require the use of organic solvents.

Another surprising advantage found in practice with medical plasters made according to the present invention is that they cause substantially no macerations, often wrongly called skin irritations. One possible explanation for this is that adhesive compositions evolved from a resin-containing mixture of aqueous plastics dispersions after drying, are to some extent hydrophilic and can therefore absorb the skin separation products present in aqueous media. This adsorption proceeds without any observable impairment of plaster properties when the plaster is used in normal conditions. Adsorption phenomena of this kind are of course out of the question with the conventional hydrophobic adhesive compositions.

The addition of resins to the mixture of aqueous plastics dispersions also considerably increases the viscosity of the resulting liquid product, so that it can be applied without any risk of soaking through the carrier and, in the case of fabric carriers, without any thickening agent having to be applied to the carrier. After the coating has dried, a pressure-sensitive adhesive film results which has greatly improved adhesive force and which is surprisingly stable in water, for the hydrophilic character of the adhesive compositions can be controlled to some extent by a choice of the resins and of their proportions.

A very wide variety of natural or synthetic resins, such as polyterpene resins, ester resins, colophony or hydrogenated or polymerised colophony or esters thereof or hydrocarbon resins, are of use for the process according to the invention, the important feature merely being that the resin or resin mixture which is added to the aqueous plastics dispersions must have a softening point plasticisation temperature of 95°C or less.

The polymers or copolymers of acrylic acid derivatives, i.e. the polyacrylic acid esters, copolymers of acrylic acid esters with other monomers copolymerisable therewith, and the

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corresponding methacrylic acid compounds, so far as their use in the process according to the invention is concerned, are not limited to those which are naturally self-sealing — i.e., which are self-sealing without an addition of a resin to make them sticky.

5 Fillers, thickening agents, medicaments, anti-ageing agents and/or stabilisers can be added to the resin-containing aqueous mixtures of the plastics dispersions to modify properties.

10 Conveniently, the aqueous plastics dispersions are worked into the resin or resin mixture in a planetary agitator with intensive agitation, although other agitators, including conventional kneaders and other mixing devices, can be used. As a rule, the aqueous plastics dispersions do not need to be heated to a relatively high temperature before processing, but preheating of the polyvinyl ether dispersion to 40 to 70°C may in some cases help to work in the resin or resin mixture which has been heated to above the softening point. The resin-containing mixture of the aqueous plastics dispersions may be applied to the carrier by any known applicator, for instance, by means of a doctor device. The application is preferably so made that the thickness of the coating after drying is from 35 to 150 g/m<sup>2</sup>.

Flexible carriers used in the process according to the invention may be of paper, all kinds of fabric, fleeces, foils of plastics or modified natural substances such as regenerated cellulose or cellulose derivatives, metal foils and fabrics of asbestos and glass fibre. There is therefore a wide choice of suitable carrier material available. If required, a priming coating or intermediate coating or layer can be used to anchor the adhesive composition more firmly on the backing, e.g. a coating of a mixture of equal parts by weight of a copolymer of butadiene and acrylonitrile and a copolymer of butadiene and styrene.

45 Conveniently, the applied coating is dried in a drying tunnel, but, if the nature of the backing permits, reel drying can be used. The dwell time in the drying tunnel depends upon temperature and therefore upon the sensitivity of the carrier material to heat, and must therefore be controlled to suit individual cases. The drying time of self-sealing compositions applied in the form of aqueous dispersion is longer than the drying time of self-sealing compositions applied in the form of a solution in a highly volatile organic solvent. However, this disadvantage is more than offset by the advantages, some of which are mentioned above, which accrue from the avoidance of using organic solvents.

60 The following examples, in which the parts given are by weight will serve to illustrate the invention: —

#### EXAMPLE 1.

65 (a) 4 parts of an abietyl alcohol ("Abitol",

ex Hercules Powder Co.) and 4 parts of a phthalic acid ester resin having a Krämer-Sarnow softening point of about 50°C ("Cellolyn 21", ex Hercules Powder Co.) are heated to about 70°C and thoroughly mixed in a planetary agitator. The resulting resin mixture has a Krämer-Sarnow softening point of 20°C. 39 parts (referred to the solids content) of an aqueous polyvinyl isobutyl ether dispersion ("Lutonal I 60 D", ex BASF, about 55% strength) are then gradually poured into the resin mixture at a temperature of about 70°C and with vigorous agitation; the temperature drops rapidly. 53 parts, referred to the solids content, of an aqueous dispersion of a polyacrylic acid ester ("Acronal 40 D", ex BASF, about 50% strength) are then added in a fine stream and with agitation.

Measurements in the Höppler viscosity meter show that the resulting resin-containing mixture of the aqueous plastics dispersions has a gel viscosity of 5060 cP and a sol viscosity of 2300 cP at a temperature of 20°C. This mixture is applied by a doctor device to a water-repellant fabric carrier in a thickness such that, after the layer has been dried in a drying tunnel, a pressure-sensitive adhesive layer in a thickness of 120 g/m<sup>2</sup> results. A medical plaster having excellent properties is thereby formed provided; it causes much less skin irritation than conventional plasters and emergency wound dressings, has very good rapid-sticking properties (49 cm.), and has an adhesive force (peel bond) on steel of 238 g/cm.

(b) By way of comparison, a mixture of aqueous plastics dispersions without an addition of resin was prepared from 42 parts, referred to the solids content, of the same aqueous polyvinyl isobutyl ether dispersion as in example (a) ("Lutonal I 60 D", ex BASF, about 55% strength) mixed with 58 parts, referred to the solids content, of the aqueous dispersion used in example (a) of a polyacrylic acid ester ("Acronal 40 D", ex BASF, about 50% strength). This mixture has a gel viscosity of 990 cP and a sol viscosity of 595 cP, as measured at a temperature of 20°C; since its low viscosity means that it is likely to soak through a fabric carrier, some sort of preliminary coating is required on the fabric carrier. Even a preliminary coating of a film-forming material did not completely obviate the risk of the composition soaking through the carrier. An adhesive strip prepared by coating a fabric with such a mixture of aqueous plastics dispersions and subsequent drying had, for the same thickness of application, poorer rapid-sticking properties (59 cm) and a lower adhesive force (186 g/cm) than the product in accordance with example 1(a).

#### EXAMPLE 2.

35 parts, referred to the solids content, of the aqueous polyvinyl isobutyl ether disper-

sion of example 1 are stirred in small batches into 17 parts of a melt, heated to 70°C, of a phthalic acid ester resin having a Krämer-Sarnow softening point of about 50°C ("Cellolyn 21", ex Hercules Powder), whereafter 48 parts, referred to the solids content, of an aqueous dispersion of any acrylic acid ester copolymer ("Acronal 500 D", ex BASF, about 50% strength) are added. A mixture having the following viscosity values is obtained.

Gel viscosity >10<sup>5</sup> cP/20°C  
Sol Sol viscosity >10<sup>5</sup> cP/20°C

A soft polyvinyl chloride foil devoid of any preliminary coating is coated with this mixture to give after drying a pressure-sensitive adhesive layer in a thickness of 58 g/m<sup>2</sup>. The anchorage of the self-sealing composition on the foil carrier, and the ageing properties of the self-sealing strip thus produced, are very good. The adhesive force on steel is 190 g/cm and the rapid-sticking value is 63 cm.

#### EXAMPLE 3

6 parts of a polyterpene resin having a melting point of 85°C and a Krämer-Sarnow softening point of 69°C ("St-5085", ex Schenectady) are mixed, as described in example 1a, at about 85°C with 39.5 parts of the aqueous polyvinyl ether dispersion and then, after considerable cooling to about room temperature, with 54.5 parts of the aqueous polyacrylate dispersion described in Example 1(a). The viscosity values of the mixture are as follows:

Gel viscosity 3450 cP/20°C  
Sol viscosity 1380 cP/20°C

This mixture is sprayed on to fibre fleece made of staple fibres obtained from viscose and being impregnated with acrylic acid ester copolymer. The average thickness of the application is about 35 g/m<sup>2</sup> after drying. A self-sealing strip which is pervious to air and to water vapour and which has excellent properties is obtained.

#### EXAMPLE 4.

6 parts of a polyterpene resin mixture having a Krämer-Sarnow softening point of 84°C (produced by mixing 4 parts of a polyterpene resin having a melting point of 85°C with 2 parts of a polyterpene resin having a melting point of 115°C) are mixed in an agitator, at about 95°C and with vigorous agitation, with 40 parts, referred to the solids content, of an aqueous polyvinyl isobutyl

ether dispersion ("Lutonal I 60 D", ex BASF, about 55% strength), the addition being made in small batches. There is then gradually added to this mixture 54 parts, referred to the solids content, of an aqueous dispersion of a polyacrylic acid ester ("Acronal 40 D", ex BASF, about 50% strength), and again with agitation. This mixture, and the mixtures which can be prepared in accordance with the following examples, can readily be applied to a variety of flexible carrier materials, i.e. a fabric carrier made from cotton or rayon staple fibre.

#### EXAMPLE 5.

To 17 parts of a polyterpene resin mixture having a Krämer-Sarnow softening point of 50°C (produced by mixing 8.5 parts of a resin having a melting point of 50°C and with 8.5 parts of a resin having a melting point of 115°C) are added at about 80°C and in exactly the same way as in Example 4, 35 parts of the aqueous polyvinyl ether dispersion described therein, followed by 48 parts of an aqueous dispersion of an acrylic acid ester copolymer ("Acronal 500 D", ex BASF, about 50% strength). The viscosity values of the mixture obtained are as follows:

Gel viscosity 1870 cP/20°C  
Sol viscosity 1160 cP/20°C

The mixture was applied to a fabric carrier made of nylon staple fibres.

#### EXAMPLE 6.

17 parts of an abietyl alcohol ("Abitol", ex Hercules Powder Co.) and 17 parts of a phthalic acid ester resin ("Cellolyn 21", ex Hercules Powder Co.) are heated to above their softening point in a planetary agitator and thoroughly mixed with one another. The resulting resin mixture has a Krämer-Sarnow softening point of 20°C. 28 parts, referred to the solids content, of an aqueous polyvinyl isobutyl ether dispersion ("Lutonal I 60", ex BASF, about 55% strength) are then gradually stirred into the resin mixture with vigorous agitation and a temperature of about 70°C, and then 38 parts, referred to the solids content, of an aqueous dispersion of a polyacrylic acid ester ("Acronal 40 D", ex BASF about 50% strength) are added similarly. A comparison between the resulting liquid mixture prepared as set forth in Example 1 (b) — i.e., without an addition of resin — is shown by the following results:

Mixture	Example 1b	Example 6
Gel viscosity	990 cP/20°C	> 1 × 10 <sup>5</sup> cP/20°C
Sol viscosity	595 cP/20°C	> 1 × 10 <sup>5</sup> cP/20°C

The two liquid mixtures are applied by a doctor device to a fabric carrier to which a coating of polyacrylic ester dispersion has previously been applied, the thickness of

application being the same in both cases. The specimens for the comparison are dried in exactly the same way. In both cases the application thickness after drying is 120 g/m<sup>2</sup>;

the application thickness of the preliminary coating is 30 g/m<sup>2</sup>.

	Product	Example 1b	Example 6
	Adhesive force on steel (g/cm)	186	286
	Adhesive force of carrier (g/cm)	48	242
5	Rapid-sticking (cm)	59	39

The words CELLOLYN, LUTONAL, ACRONAL and COLLOLYN used herein are Registered Trade Marks.

#### WHAT WE CLAIM IS:—

- 10 1. A process for the production of pressure sensitive adhesive strips and foils which comprises mixing with vigorous agitation a solid, water-insoluble resin or mixture of such resins having a softening point of 95°C or less,
- 15 heated to a temperature above the said softening point, with aqueous dispersion of a non-toxic and chemically neutral vinyl ether polymer or vinyl ether copolymer, mixing the mixture obtained with an aqueous dispersion
- 20 of a polymer or copolymer of an acrylic acid derivative selected from polyacrylic acid esters, polymethacrylic acid esters, and copolymers of acrylic acid esters or methacrylic acid esters with other monomers copolymerisable
- 25 therewith, applying the mixture thus obtained as a layer on a flexible carrier material and drying the layer thus obtained.
2. A process according to claim 1 wherein the aqueous dispersion of vinyl ether polymer or copolymer is heated to a temperature
- 30 of 40 to 70°C.
3. A process according to claim 1 or 2, wherein 2 to 50 parts by weight of the resin or resin mixture are mixed with from 20
- 35 to 50 parts by weight, referred to the solids content, of the aqueous dispersion of the vinyl ether polymer or vinyl ether copolymer, and

the mixture is mixed with from 25 to 75 parts by weight, referred to the solids content, of an aqueous dispersion of the said polymer or copolymer of an acrylic acid derivative.

4. A process according to claim 3 when 5 to 25 parts by weight of the resin or resin mixture are employed.

5. A process according to any of the preceding claims wherein fillers, thickening agents, medicamental substances, anti-ageing agents and/or stabilisers are included in the mixture applied to the carrier material.

6. A process according to any of claims 1—5 wherein the carrier material is a strip or sheet of paper, plastics foils or textile or glass fabric.

7. A process according to any of claims 1—6 wherein the mixture is applied to the carrier material at a dried weight of 35 to 150 g/m<sup>2</sup>.

8. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific examples.

9. Self-sealing strips, foils and medical plasters, when prepared by any of the processes in any of claims 1 to 7 or described in Examples 1(a), 2 and 6.

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